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Top Ten Reasons for DEOX as a Front End to Pyroprocessing

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BACKGROUND

A front end step is being considered to augment chopping during the treatment of spent oxide fuel by pyroprocessing. The front end step, termed DEOX for its emphasis on decladding via oxidation, employs high temperatures to promote the oxidation of UO_2 to U_3O_8 via gaseous oxygen. During oxidation, the spent fuel experiences a 30% increase in lattice structure volume resulting in the separation of fuel from cladding with a reduced particle size. A potential added benefit of DEOX is the removal of fission products, either via direct release from the broken fuel structure or via oxidation and volatilization by the high temperature process.

Fuel element chopping is the baseline operation to prepare spent oxide fuel for an electrolytic reduction step. Typical chopping lengths range from 1 to 5 cm for both individual elements and entire assemblies. During electrolytic reduction, uranium oxide is reduced to metallic uranium via a lithium molten salt. An electrorefining step is then performed to separate a majority of the fission products from the recoverable uranium.

Although DEOX is based on a low temperature oxidation cycle near 500°C, additional conditions have been tested to distinguish their effects on the process.[1] Both oxygen and air have been utilized during the oxidation portion followed by vacuum conditions to temperatures as high as 1200°C. In addition, the effects of cladding on fission product removal have also been investigated with released fuel to temperatures greater than 500°C.

REASONS FOR DEOX DURING PYROPROCESSING

Since DEOX is being considered for inclusion in the pyroprocessing flowsheet, a comparison of chopping versus chopping with DEOX is discussed in three primary areas. The three areas encompass particle size, fuel separation from the zircaloy cladding or decladding, and potential fission product release. The ten advantages of including DEOX with chopping are given.

1) Increased Reduction Rates for Finer Particles

According to tests performed on laboratory-scale electrolytic reduction equipment [2], the reduction rate of uranium oxide can be increased by a factor of three for crushed versus uncrushed spent oxide fuel. The uncrushed fuel was retained by cladding during these tests while the crushed was declad. The DEOX process is expected to deliver a reduced particle size similar in characteristics to the crushed fuel.

2) Difficulty with Very Fine (<10 um) Particles

During the chopping operation, small fuel fragments are dislodged from the cladding of which, a fraction (5-10% of the initial fuel) of the particles are less than 10 um. These particles present problems in containment during electrolytic reduction due to limitations in porous crucible materials. The DEOX process can be tailored to produce particles larger than 10 um which would be more easily contained.

3) Minimal Contamination of Hot Cell due to Dusting

The particles less than 10 um have the potential to spread contamination throughout the hot cell environment during normal handling operations. These fines would be eliminated by the DEOX process.

4) Carryover of Salt to Electrorefining is Reduced

The amount of salt carried over from the electrolytic reduction step to electrorefining is dependent on the initial particle size before reduction. Smaller particles have more salt entrained/occluded than larger particles.[2] Thus, adjustments to the electrorefiner salt can be minimized by avoiding fines and salt carryover.

5) Potential Disposition of Cladding

Based on cladding samples taken following DEOX testing, only 2 um of the inner clad layer would need to removed to meet the TRU alpha-nuclide waste criteria of less than 100 nCi/g. Cladding samples were also taken prior to DEOX testing which indicate a significantly wider distribution of TRU in accordance with other investigators.[3] Thus, less of the inner layer would need to be removed following DEOX as opposed to just a chopping operation.

6) Effect of Cladding on Electrolytic Reduction

Two potential reactions can be avoided by keeping cladding out of the electrolytic reduction vessel, i.e. using DEOX as a cladding separation step. The first reaction of

metallic lithium with oxidized cladding would cause a loss of lithium from the uranium reduction reaction. The second would be the reaction of the zircaloy cladding with uranium oxide resulting in contamination of the salt with zirconium oxide.

7) Effect of Cladding on Electrorefining

From previous testing, the amount of lithium oxide carried over to the electrorefiner was increased by at least a factor of two when cladding was included during the electroreduction step.[2] This carryover results in losses at the electrorefiner of uranium trichloride which must be replenished since it is the primary fission product oxidant.

8) Release of Volatile Fission Products for Recapture

The volatile fission products of interest in terms of containment issues during pyroprocessing are tritium, krypton, and potentially xenon. It is expected that these volatiles would be released during the chopping, electrolytic reduction, and electrorefining steps to the hot cell atmosphere. Nearly complete removal of these fission products has been achieved by the OREOX process which is analogous to DEOX.[4] With DEOX, the release and potential capture of these volatile fission products during a single process step would simplify the overall process.

9) Release of Semi-Volatile Fission Products

During DEOX processing, several semi-volatile fission products are either oxidized to a volatile species or released such that their removal may be beneficial to flowsheet development efforts for pyroprocessing.[5] The semi-volatiles removed during DEOX are cesium, iodine, tellurium, and the noble metals (viz. technetium, ruthenium, rhodium, and molybdenum). The removal of these fission products in a head-end treatment step may increase the process efficiency of both electroreduction and electrorefining while decreasing the waste-loading and thus, disposition options.

10) Selective Trapping of Volatile Fission Products

Recent research has revealed the ability to trap and isolate specific volatile fission products on separate filter media during DEOX.[6] Fission products that have been effectively trapped include cesium, technetium, and iodine. The selective capture of these fission products up front may have a significant impact on repository issues.[7]

REFERENCES

1. B.R. WESTPHAL et al., "Effect of Process Variables During the Head-End Treatment of Spent Oxide Fuel", *Nucl. Tech.*, in publication.
2. E.J. KARELL and K.V. GOURISHANKAR, *Electrometallurgical Treatment of Oxide Spent Fuel – Engineering-Scale Development*, Proc. DOE Spent Nucl. Fuel and Fissile Mtls. Mgt., Charleston, SC, Vol. 2, p. 682, ANS (1998).
3. I.H. JUNG, J.M. SHIN, H.H. LEE, J.J. PARK, and M.S. YANG, "Investigation of PWR Hull with a View to Downgrade", *Sep. Sci. Tech.*, **41**, *10*, p. 2097 (2006).
4. K.C. SONG, G.I. PARK, J.W. LEE, J.J. PARK, and M.S. YANG, "Fractional Release Behavior of Volatile and Semi-Volatile Fission Products during a Voloxidation and OREOX Treatment of Spent PWR Fuel", *Nucl. Tech*., in publication.
5. B.R. WESTPHAL, K.J. BATEMAN, R.P. LIND, K.L. HOWDEN, and G.D. DEL CUL, *Fission Product Removal from Spent Oxide Fuel by Head-End Processing*, Proc. Global 2005, Tsukuba, Japan, AESJ, (2005).
6. B.R. WESTPHAL, K.J. BATEMAN, R.P. LIND, and D.L. WAHLQUIST, "Recent Progress in the DEOX Process", *Trans. Am. Nucl. Soc*., **94**, p. 103 (2006).
7. R.A. WIGELAND, T.H. BAUER, T.H. FANNING, and E.E. MORRIS, "Separations and Transmutation Criteria to Improve Utilization of a Geological Repository", *Nucl. Tech*., **154:1**, p. 95 (2006).